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54 Method for the preparation of gels capable of taking up and releasing water in a reversible manner from clay minerals and polymers.

57 A method of making a gel capable of reversibly absorbing and releasing water is described in which a clay mineral (a smectite or a swellable silicate), that has optionally been activated by no more than 1% of an activator (an alkali metal or ammonium salt having an anion that forms an insoluble precipitate with alkaline earth metal ions), is mixed with a water soluble polymer capable of reacting with the clay (e.g. polymers containing -COOH, -COO<sup>-</sup> M<sup>+</sup> (where M<sup>+</sup> is a monovalent cation), -CONH<sub>2</sub>, -OH and/or -C-O-C- groups). This mixture can then be mixed with an activator (as described above) and optionally some water to form the gel. The final addition of activator can be performed on site so that the whole gel need not be transported to the site.

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## Description

**METHOD FOR THE PREPARATION OF GELS CAPABLE OF TAKING UP AND RELEASING WATER IN A REVERSIBLE MANNER FROM CLAY MINERALS AND POLYMERS**

5 The invention relates to an improved method for the preparation of gels with stable structure, capable of taking up and releasing water in a reversible manner, from clay minerals and polymers.

It is known from Hungarian patents Nos. 186,325 and 189,280 that when a thixotropic swellable smectite of three-layer structure and/or a swellable chain silicate is reacted in activated state or during activation with a water soluble polymer capable of reacting with said clay mineral, stable chemical bonds are formed between the clay mineral and the polymer. The clay mineral, which is disintegrated mainly to its elementary lamellae or chains during activation, forms chemical bonds with the polymer on its reactive sites, whereupon the elementary lamellae or chains of the clay mineral "get stringed" on the polymer, and a stable gel structure is formed. This gel, unlike the starting clay mineral, is no longer thixotropic and does not peptize upon the effect of water, but when contacted with water it swells easily and takes up and releases water in a reversible manner. Such gels can be applied to advantage in the production of water-tight layers, furthermore to improve the water household of soils.

As mentioned in the cited references, in order to obtain a stable, irreversibly fixed gel structure capable of taking up and releasing water in a reversible manner, it is of crucial importance that the clay mineral should be reacted with the polymer in activated state or during activation. Otherwise, i.e. when a cluster-like clay mineral incompletely disintegrated to elementary lamellae or chains is applied as starting substance, the clay mineral packages react with the polymer only on their surface and enter a loose sorption interaction with the polymer, but only a very few chemical bonds are formed, if any. When a non-activated clay mineral is reacted with a water-soluble polymer, a product consisting of inorganic and organic macromolecules is formed, the structure and gelling properties of which are determined primarily by the given characteristics of the inorganic component (i.e. the clay mineral), the organic component only modifying these properties to a greater or lesser extent. As an example, when a thixotropic, swelling clay mineral of three-layer structure is reacted in non-activated state with the polymer, the resulting product still remains thixotropic; the polymer present modifies only certain other properties (e.g. elasticity, strength, swell-ability, etc.) of the gel to a greater or lesser extent.

Gels with highest quality are obtained when an activated clay mineral is reacted with a water soluble polymer in a relatively thin suspension; otherwise, owing to the quick reaction between the polymer and the clay mineral, the appropriate distribution of the polymer and the most complete reaction of the reactive sites cannot be ensured. Thus the gels with stable structure, capable of taking up and releasing water in a reversible manner, are formed initially in a thin suspension with high water content. The transport of such gels is rather expensive, and these gels should be subjected to a lengthy and energy-intensive drying operation in order to remove or reduce their water content. Although a thick mass of activated clay mineral can also be applied as starting substance in gel formation, the gels formed from such thick masses are generally poorer in quality than those formed from thin suspensions, and specific mixing apparatuses with very high performance are required to react the thick activated clay mineral mass with the polymer. Consequently, the apparatus and energy demands of this operation are high, which renders the procedure less economic.

Therefore there is a need for an improved method which enables one to avoid the disadvantages mentioned above and to produce gels with high quality in a more economical way than before.

Now it has been found, unexpectedly, that when a clay mineral is reacted in non-activated or partly activated state with a water soluble polymer in an amount required for gel formation, and the resulting clay mineral/polymer complex is activated subsequently, preferably directly before its use, the clay mineral is still able to disintegrate into its elementary lamellae or chains upon the subsequent activation procedure, and the liberated reactive sites of the clay mineral react directly with the polymer present, whereupon a stable gel structure fixed irreversibly by chemical bonds and capable of taking up and releasing water in a reversible manner is formed. This recognition is very surprising, since one had to expect that the polymer present in the clay mineral/polymer complex, bound to the surface of the clay mineral packages by sorption or loose chemical bonds, would completely impede the subsequent activation procedure.

Based on the above, the invention relates to an improved method for the preparation of gels capable of taking up and releasing water in a reversible manner from clay minerals and polymers. According to the invention one proceeds as follows:

A clay mineral in non-activated state or optionally pre-treated with up to 1.0 % by weight of an activating agent, calculated for the weight of the clay mineral,

55 a) is treated in a suspension containing at least 8 % by weight, preferably 10-50 % by weight, of dry substance with at least 0.6 % by weight, preferably 1.5-15 % by weight, of a water soluble polymer capable of reacting with the clay mineral, calculated for the dry substance content of the suspension, and the resulting suspension of a clay mineral/polymer complex is admixed, preferably directly before use, with at least 0.5 % by weight, preferably 1.0-5.0 % by weight, of an activating agent, calculated for the clay mineral content; or

60 b) is treated as a mass with a dry substance content of at least 15 % by weight, preferably 60-70 % by weight, with at least 0.6 % by weight, preferably 1.5-15 % by weight, of a water soluble polymer capable of

reacting with the clay mineral, calculated for the dry substance content, then, if necessary, the water content is lowered to or below 40 % by weight, the resulting mass is optionally granulated, and the resulting clay mineral/polymer complex is admixed, preferably directly before use, with at least 0.5 % by weight, preferably 1.0-5.0 % by weight, of an activating agent, calculated for the weight of the clay mineral; or

c) is treated as a mass with a dry substance content of at least 8.0 % by weight, preferably 10-70 % by weight, with at least 0.6 % by weight, preferably 1.5-15 % by weight, of a water soluble polymer capable of reacting with the clay mineral, calculated for the dry substance content, the resulting clay mineral/polymer complex is dried to a water content of not more than 20 % by weight taking care that in the drying operation the surface of the dry substance should not warm to a temperature exceeding 150°C for a prolonged period of time, if desired, the resulting dry substance is powdered or granulated, and the resulting clay mineral/polymer complex is admixed, preferably directly before use, with at least 0.5 % by weight, preferably 1.0-5.0 % by weight, of an activating agent, calculated for the weight of the clay mineral, in the presence of water.

The term "clay mineral" as used in the specification and claims covers solely swellable smectites of three-layer structure and/or swellable chain silicates, furthermore rocks, mine products and artificial mixtures comprising such clay minerals in an amount of at least 10 % by weight. Examples of the clay minerals usable in the method of the invention are montmorillonite, beidellite, hectorite, nontronite, illite, alleverdite and palygorskite, whereas an example of the clay mineral-containing rocks is bentonite.

Any alkali metal or ammonium salt with an anion which forms water-insoluble precipitate with alkaline earth metal ions can be applied as activating agent. Of the activating agents e.g. sodium carbonate, mono-, di- and trisodium phosphates, tripolyphosphate, sodium sulphate, lithium carbonate, lithium phosphates, ammonium carbonate, ammonium phosphates and mixtures thereof are mentioned. According to a particularly preferred method an overactivated smectite (i.e. a smectite treated with a surplus amount of activating agent) or such a smectite-containing rock (e.g. overactivated bentonite) is applied as activating agent.

Pre-activated smectites (i.e. smectites pre-treated with a minor amount of activating agent) can also be applied as starting substances in the method of the invention, if such materials are available. However, in order to form a final gel with stable structure, capable of taking up and releasing water in a reversible manner, it is not necessary to use pre-activated smectites, since even the non-activated smectites can react completely with the polymer upon the subsequent activation procedure.

The water soluble polymers capable of reacting with clay minerals are known per se; of them water soluble polymers containing -COOH, -COO-M<sup>+</sup> (M<sup>+</sup> is a monovalent cation), -CONH<sub>2</sub>, -OH and/or -C-O-C- groups as functional groups are to be mentioned. Polymers with modified amido groups (wherein the amido group is converted into quaternary ammonium group) can be used as well. Examples of these polymers are polyacrylamide, polymethacrylamide, acrylamide - acrylic acid copolymers, hydrolysed acrylamide - acrylic ester copolymers, vinyl alcohol - acrylic acid copolymers, polyvinyl alcohols, hydrolysed polyvinyl esters, polyethylene oxides, water soluble polysaccharides, etc., and mixtures of these homo- and copolymers. Graft copolymers can also be applied, of them copolymers containing acrylic acid, methacrylic acid, acrylamide and/or methacrylamide side chains grafted onto a polysaccharide chain are to be mentioned.

The molecular weight of the polymers usable in the method of the invention may vary generally between 50,000 and 20,000,000, preferably between 300,000 and 10,000,000. According to our experiences the greater the molecular weight of the polymer, the smaller amount of polymer is required for the reaction.

It is an essential measure of the method according to the invention that the clay mineral/polymer complex is subsequently activated, i.e. the clay mineral/polymer complex or its suspension is admixed with an activating agent. Any of the activating agents listed above can be applied for this purpose. This operation is performed in the presence of water. It is preferred to form suspensions comprising at least 6 % by weight of dry substance. One can proceed in such a way that the clay mineral/polymer complex is suspended in water and the solid activating agent is added to this suspension. According to another method the clay mineral/polymer complex is added to an aqueous solution or suspension of the activating agent. The amount of activating agent to be introduced varies with the type of the starting clay mineral; it is, however, absolutely necessary to use at least 0.5 % by weight of an activating agent, calculated for the weight of the starting clay mineral. The activating agent is used generally in an amount of 1-5 % by weight calculated for the weight of the starting clay mineral. Upon admixing the clay mineral/polymer complex with the activating agent the smectite packages coated with polymer start to swell, then they disintegrate at least in part into their elementary lamellae or lamellae packages, whereupon fresh surface points capable of reacting with the polymer (binding sites) liberate in a great amount. The newly liberated binding sites react immediately with the polymer present, whereupon a stabilized gel structure capable of taking up and releasing water in a reversible manner is formed.

A major advantage of the method of the invention is that there is no need for utilizing this suspensions, since the non-activated clay mineral can be treated with the polymer even as a thick mass. Significantly less energy is required to admix a thick mass of a non-activated clay mineral with a polymer than it would be required when applying a thick mass of an activated clay mineral as starting substance. The resulting clay mineral/polymer complexes or the suspensions containing them are stable, they can be stored without any change for a prolonged period of time, and their transport is much less expensive than that of the thin suspensions comprising generally less than 10 % by weight of dry substance. These clay mineral/polymer complexes and the suspensions containing them can be activated very easily directly at the place of use; it is sufficient to

apply e.g. a simple concrete mixer for admixing the clay mineral/polymer complex with the activating agent. Some properties of the resulting stabilized gel (e.g. the gelling time) can be varied by varying the nature and amount of the activating agent; thus gels with varying properties adaptable to local requirements can be prepared from one and the same starting substance.

5 The invention is elucidated in more detail by the aid of the following non-limiting Examples.

Example 1

10 5 litres of an aqueous suspension with a dry substance content of 40 % by weight were prepared from bentonite originated from Istenmezeje, Hungary (sold by Országos Érc- és Ásványbányák Vállalat, Mád, Hungary). The suspension was divided into five equal parts, and then the polymers (and optionally the activating agents used for preactivation) listed in Table I were admixed with the individual portions in the amounts listed in Table I. The suspensions were stirred for 3 minutes with an Ultraturrax stirrer and then allowed to stand. The individual samples were divided into two equal parts, and the activating agents listed in Table I were admixed with the samples one hour or one month after their preparation, respectively.

15 Gels with stable structure, capable of taking up and releasing water in a reversible manner, were formed from each of the suspension samples. The formation of stable gel structure is verified by the fact that the resistance of medium of the individual suspension samples rose to 4-10- times the initial value upon admixing them with the activating agent. The properties of the resulting gels did not vary with the storage period of the suspension before admixing it with the activating agent.

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Table I

Sample No.	Preactivating agent Type	Amount*	Polymer Type	Amount*	Activating agent Type	Amount*
1	-	-	Polyacrylamide	5.8	Sodium carbonate	2.6
2	Trisodium phosphate	0.4	Acrylic acid - acrylamide copolymer	6.5	1:1 mixture of sodium carbonate and trisodium phosphate	2.3
3	1:1 mixture of sodium carbonate and trisodium phosphate	0.3	A-100**	3.4	Sodium carbonate	2.2
4	Lithium carbonate	0.5	A-110***	6.8	Lithium carbonate	2.2
5	Disodium hydrogen phosphate	0.4	Robofloc F50***	2.5	Triphosphosphate	3.0

\* % by weight, calculated for the weight of the dry substance

\*\* Hydrolysed polyacrylamide, produced by American Cyanamid Co.

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**Example 2**

Crude calcium bentonite originating from Bavaria and illite originating from Füzérradvány, Hungary (sold by Országos Érc- és Ásványbányák Vállalat, Mád, Hungary) were admixed in a weight ratio of 1:1, and a suspension with a dry substance content of 35 % by weight was prepared from the mixture. Thereafter 0.5 % by weight of a 1:1 mixture of sodium carbonate and trisodium phosphate, calculated for the weight of the dry substance, was added to the suspension under intense stirring. After 5 minutes of stirring 6.5 % by weight of an acrylamide - acrylic acid copolymer (average molecular weight: 1,500,000), calculated for the dry substance content, were added to the suspension, and stirring was continued for 10 minutes.

The resulting suspension was allowed to stand for one day, thereafter diluted with an equal amount of water under intense stirring, and 3.0 % by weight of sodium carbonate, calculated for the dry substance content, were added to the suspension. The suspension was stirred for 10 minutes in a Labomix kneading-mixing apparatus. A gel with stable structure was formed; the resistance of medium of the suspension rose to 5.5-times the initial value.

**Example 3**

Freshly mined bentonite originating from Istenmezeje (Hungary) with a dry substance content of 72 % by weight (sold by Országos Érc- és Ásványbányák Vállalat, Mád, Hungary) is admixed with water in a laboratory kneading-mixing apparatus to obtain a mass with a water content of 60 % by weight. The resulting mass is passed through three laboratory roller mills with gradually decreasing slot widths to reduce the particle size of the inert impurities present (e.g. sand) below 0.1  $\mu\text{m}$ .

500 g of a mass pre-treated as described above are put into a laboratory kneading-mixing apparatus, and 100 g of an aqueous polyacrylamide solution with a dry substance content of 5 % by weight (average molecular weight of the polymer:  $3 \times 10^6$ ) are added in portions. The mass is kneaded for 2 minutes.

100 g of the resulting paste-like mass are pulled to small pieces, the small pieces are added to 200 g of water in a household mixer, and the mixture is stirred for 2 minutes. Thereafter 3 % by weight of sodium carbonate, calculated for the dry substance content, are introduced. After 2 minutes of stirring a stable gel of excellent quality is formed from the mixture.

**Example 4**

100 g of a paste-like clay mineral/polymer mass prepared as described in Example 3 are filled into a laboratory mixer, and then 3 % by weight of trisodium phosphate, calculated for the dry substance content, are added to the mass as a concentrated aqueous solution. After 2 minutes of stirring the resistance of medium of the mass rises to eight times the initial value, which indicates gel formation. The resistance of medium of the resulting gel is higher by 70 % than that of a gel prepared otherwise in the same way from the same materials but using an activated clay mineral as starting substance.

**Example 5**

Freshly mined bentonite originating from Várkenő (Hungary), containing 75 % by weight of dry substance, is comminuted by passing through an edge runner, and then the mass is passed through two laboratory roller mills with gradually decreasing slot widths to adjust the particle size of the solids below 0.1  $\mu\text{m}$ . Thereafter the bentonite is filled into a clay extruder, water is added to it in an amount to reach a water content of 45 %, and then 20 % by volume of an aqueous hydrolysed polyacrylamide (average molecular weight:  $1.5 \times 10^6$ , degree of hydrolysis: 5 %) solution with a dry substance content of 2.5 % by weight, calculated for the volume of the bentonite mass, is admixed with the bentonite mass.

The resulting mixture is passed through a cylindrical head 2 mm in diameter, and the extruded material is cut into small cylinders 5 mm in length. The resulting granules are dried in a drum dryer; hot (300°C) flue gas introduced in a countercurrent stream is used as drying agent. The contact period of the flue gas and the granules is adjusted to about 5 minutes; in this way the surface of the granules cannot reach a temperature exceeding 150°C for a prolonged period of time. Hard, brittle grains are obtained with a humidity content of about 10 % by weight.

The dried grains are comminuted in a hammer mill, and the comminuted particles are divided into two fractions by sieving. The course fraction, comprising grains with an average diameter of 0.3-1 mm, is a free-flowing granulate easy to sprinkle. The fine fraction is a fine powder comprising particles with an average diameter less than 0.3 mm.

8 g of a powdery clay mineral/polymer complex obtained as described above are sprinkled into a solution of 0.16g of sodium carbonate in 92 g of water under steady stirring. The particles of the clay mineral/polymer complex start to swell intensely, and after about 10 minutes of stirring a pappy gel mass is formed. Stirring is stopped and the mixture is allowed to stand. After about 1-2 hours of standing a completely homogeneous gel, capable of taking up and releasing water in a reversible manner, is formed.

## Claims

1. A method for the preparation of gels capable of taking up and releasing water in a reversible manner from clay minerals and polymers, characterised in that a clay mineral in non-activated state or optionally pre-treated with up to 1.0 % by weight of an activating agent, calculated for the weight of the clay mineral,

a) is treated in a suspension containing at least 8 % by weight, preferably 10-50 % by weight, of dry substance with at least 0.6 % by weight, preferably, 1.5-15 % by weight, of a water soluble polymer capable of reacting with the clay mineral, calculated for the dry substance content of the suspension, and the resulting suspension of a clay mineral/polymer complex is admixed, preferably directly before use, with at least 0.5 % by weight, preferably 1.0-5.0 % by weight, of an activating agent, calculated for the clay mineral content; or

b) is treated as a mass with a dry substance content of at least 15 % by weight, preferably 60-70 % by weight, with at least 0.6 % by weight, preferably 1.5-15 % by weight, of a water soluble polymer capable of reacting with the clay mineral, calculated for the dry substance content, then, if necessary, the water content is lowered to or below 40 % by weight, the resulting mass is optionally granulated, and the resulting clay mineral/polymer complex is admixed, preferably directly before use, with at least 0.5 % by weight, preferably 1.0-5.0 % by weight, of an activating agent, calculated for the weight of the clay mineral; or

c) is treated as a mass with a dry substance content of at least 8.0 % by weight, preferably 10-70 % by weight, with at least 0.6 % by weight, preferably 1.5-15 % by weight, of a water soluble polymer capable of reacting with the clay mineral, calculated for the dry substance content, the resulting clay mineral/polymer complex is dried to a water content of not more than 20 % by weight taking care that in the drying operation the surface of the dry substance should not warm to a temperature exceeding 150°C for a prolonged period of time, if desired, the resulting clay mineral/polymer complex is powdered or granulated, and the resulting clay mineral/polymer complex is admixed, preferably directly before use, with at least 0.5 % by weight, preferably 1.0-5.0 % by weight, of an activating agent, calculated for the weight of the clay mineral, in the presence of water.

2. A method as claimed in claim 1, characterised in that sodium carbonate, mono-, di- and trisodium phosphate, tripolyphosphate, lithium carbonate, a lithium phosphate, sodium sulphate, ammonium carbonate, an ammonium phosphate and/or an overactivated smectite is applied as activating agent.

3. A method as claimed in claim 1 or 2, characterised in that the clay mineral/polymer complex is treated with the activating agent as a suspension containing at least 6 % by weight of dry substance.

4. A method as claimed in any of claims 1 to 3, characterised in that the clay mineral/polymer complex is suspended in water, and the activating agent is added to the suspension.

5. A method as claimed in any of claims 1 to 3, characterised in that the clay mineral/polymer complex is added to an aqueous solution or suspension of the activating agent.

6. A mixture comprising (I) a clay material that has been optionally partly activated by up to 10% by weight of an activating agent (calculated on the weight of the clay mineral) and (II) at least 0.6% by weight, and preferably 1.5 to 15% by weight, (calculated on the weight of the clay mineral) of a water-soluble polymer capable of reacting with the clay mineral, which mixture is capable of forming a gel that can absorb and release water upon addition of 1 to 5% by weight (based on the weight of the clay mineral) of an activating agent.

7. A mixture as claimed in claim 6, having a water content of less than 40% by weight and preferably less than 20% by weight.



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number

EP 89 30 3037

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	US-A-4 600 744 (LIBOR) * Column 2, line 45 - column 3, line 63; column 7, line 60 - column 8, line 67 *	1	C 09 K 17/00
Y	EP-A-0 072 213 (UNILEVER) * Page 2, lines 2-34; claims 1-13 *	1	
A	---	7	
A	US-A-4 242 140 (ALTHER) * Columns 7-8; claims 1-18 *	2	
A	EP-A-0 244 981 (ALLIED COLLOIDS) * Page 8, claims 1-10 *	1	
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			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 09 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04-07-1989	Examiner WENDLING J.P.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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